

Respirometric Evaluation of the Biodegradability of Films of PE/PHBV Blends

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Abstract

Films of Polyethylene (PE), Poly (3-hydroxybutyrate-co-hydroxyvalerate) (PHBV, 18% HV) and PE/PHBV blends containing 10 and 30% of PHBV were buried in soil for 180 days to evaluate their biodegradability through the respirometry test. The biodegradation of the films was investigated by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The biodegradation rate was found to be increased in blends containing larger proportions of biodegradable polymer, due to increasing interphase (intermediate regions) between the two polymers. Therefore, the biodegradation rate was proportional to the amount of biodegradable polymer phase (PHBV) in contact with the PE.

Keywords

Biodegradation; PE; PHBV

Introduction

The extensive and increasing use of polymer materials with their wide range of applications in various areas has created a significant rise in plastic waste discarded in the environment, encouraging the scientific community to investigate new polymer materials, such as blends between degradable and synthetic polymers [Rosa 2009, Gonçalves 2009, Santana 2012, Campos 2010, Shah 2008, Luckachan 2011].

Polyethylene (PE) is a synthetic polymer widely used on a commercial scale, especially in the packaging industry due to its easy production, excellent chemical resistance and processability [Kyrikou 2011]. After used up, PE materials are discarded into different ecosystems, where they cause numerous problems associated with the accumulation of solid waste due to their inertia and resistance to microorganisms.

One option to reduce the accumulation of solid waste is the use of biodegradable polymers that are accessible to microbial assimilation. Polyhydroxyalkanoates (PHAs), whose mechanical and thermal properties are similar to those of

conventional thermoplastics, are polyesters produced in nature by bacteria. A representative the family of PHAs is Poly (3-hydroxybutyrate-co-hydroxyvalerate) (PHBV), whose desirable mechanical performance and rapid biodegradation in different natural environments make it an attractive material [Hermida 2009].

The biodegradation of polymers is influenced by their chemical structure, especially the presence of functional groups, their hydrophobic-hydrophilic balance, the presence of highly ordered structures such as crystallinity and orientation, and other morphological properties [Oldak 2005, Gu 2003]. Most of the tests employed to monitor polymer biodegradation are based on the determination of CO₂ produced by microbial respiration [Calmon 2000, Krzan 2006, Bastioli 2005], combined with measures of structural changes (FTIR) and morphology (XRD) of polymers [Starka 2004, Furukawa 2007, Conti 2006, Kunioka 1989].

The polymer blends obtained by mixing synthetic and biodegradable polymers can allow for good interaction with microorganisms in the environment. This study investigated the biodegradation of PE/PHBV blends containing 10 and 30% PHBV, based on respirometric tests, FTIR, XRD and SEM.

Materials and Methods

The polymers used in this study were LDPE with a density of 0.922 g/cm³ and MFI (melt flow index) of 3.8 g/10 min (Braskem PE BP-681/59) and PHBV (Mw = 237,500, 18 mol% HV content).

The polymers and blends were mixed for 15 min in a Thermo Haake rheometer operated at 170°C and 60 rpm. The polymer films were compression-molded for 3 min at 170°C between two aluminum sheets in a hot hydraulic press, under a pressure of 8.7 MPa to obtain 100 µm thick films. The films were then allowed to

cool to ambient temperature (25-26°C).

The polymer films were subjected to respirometry testing to quantify the production of carbon dioxide released by microbial respiration and to evaluate their biodegradation, according to the ISO 14855 standard [Weng 2011]. Biometer flasks used as originally suggested by Bartha and Pramer [Bartha 1965], each containing 50 g of soil + polymer sample (duplicate) were incubated at $28^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 180 days. CO_2 production was measured volumetrically at intervals of approximately 24 h.

Infrared spectra of the blend and pure films were recorded in a Shimadzu Prestige-21 FTIR spectrometer operated at a spectral resolution of 4 cm^{-1} for all the samples, with scanning performed at room temperature before and after the respirometric test.

X-ray diffraction (XRD) measurements were taken using a RIGAKU RU-200B diffractometer (belonging to IFSC/USP, São Carlos, SP, Brazil) operated at 50 kV and 100 mA using a $\text{CuK}\alpha$ radiation wavelength of 1.54 Å as the X-ray source. Diffraction patterns were recorded in the range of $2\theta = 10\text{--}35^{\circ}$ at a scan speed of $0.36^{\circ}/\text{min}$ at room temperature.

The changes occurring on the surface of the polymer films were analyzed under a Zeiss DSM 940-A scanning electron microscope, using an acceleration voltage of 4 keV.

Results

A respirometer is used to measure the volume of CO_2 produced by the respiration of microorganisms during aerobic biodegradation [Kijchavengkul 2006]. The evolution of CO_2 , a direct parameter to verify polymer mineralization, is therefore a useful way to determine the biodegradability of polymer material [Calmon 2000, Bastioli 2005, Solaro 1998].

Fig. 1 shows the percentage of biodegradation of polymer films based on CO_2 production. PHBV films incubated for 6 months presented the highest biodegradation rate, which was evidenced by the impossibility to detect the films in the soil after this experimental period due their complete disintegration. The PHBV films became mineralized by the action of the microorganisms in the soil. This was demonstrated earlier by Weng et al. [Weng 2011] who studied the biodegradation of PHAs (PHB, PHBV (40, 20 and 3 mol% HV) and P(3HB, 4HB) (10% mol 4HB) under controlled composting conditions, and found that 50% of the films were undetectable after 20 days due to

their biodegradation by enzyme catalyzed erosion occurring from the surface toward the core of the films.

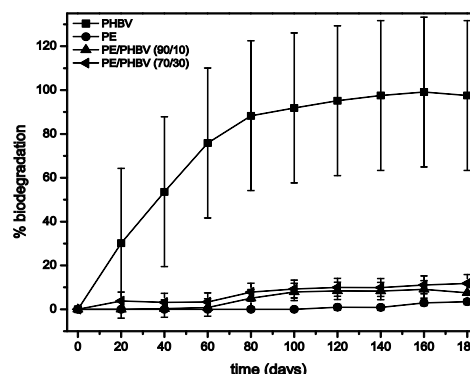


FIG. 1 PERCENTAGE OF FILMS BIODEGRADATION FROM RESPIROMETRY ANALYSIS, WITH AVERAGE STANDARD DEVIATION.

In this work, the PE films started to biodegrade after 120 days, keeping about 3.5% of biodegradation at the end of the experiment. The long period of latency is attributed to the properties of the material, such as hydrophobicity and degree of crystallinity [Roy 2008] which are important factors in biodegradation due to the effect of water and enzyme accessibility [Vilaplana 2010]. Corti et al. [2010] found that the production of CO_2 in preoxidized PE samples containing prooxidant additives was greater than that in films without these additives. This finding was explained by the ability of fungi to use the products of oxidation as sources of carbon.

The PE/PHBV 90/10 and 70/30 blends showed 7 and 12% biodegradation, respectively, in the same period, with greater biodegradation of the blend containing the higher proportion of biodegradable polymer (70/30).

CO_2 evolution, an efficient method to assess the biodegradation of polymer films, is directly related with the morphology of biodegraded polymer films, as illustrated in the following FTIR, XRD and SEM images.

Infrared spectroscopy is a versatile technique to determine compositions and macromolecular configurations, and to compare morphologies against parameters such as crystallinity (crystallinity index) and phase segregation of polymer systems [Gulmine 2002, Sato 2011]. However, the crystallinity index does not represent an absolute degree of crystallinity [Bloembergen 1986].

Fig. 2 shows FTIR spectra of the untreated PHBV and

biotreated films. The spectra were normalized using the band at 1380 cm^{-1} as internal standard, which is assigned to CH_3 symmetric deformation, independent of crystallinity [Singh 2008]. The spectra of the PE and blend films after 180 days of biotreatment were normalized in relation to the band at 1465 cm^{-1} (CH_2) [Sudhakar 2008].

After the respirometric test, the PE showed 8% increase in the intensity of the band at 1377 cm^{-1} , which was attributed to the percentage of short chain branching (methyl, butyl and hexyl) of the PE bonds, indicating breaks in these chains [Quental 2005].

After the respirometric test on the PHBV and blends, several changes were detected in the bands at 1278 and 1184 cm^{-1} which were attributed, respectively, to CH_2 vibrations and C-O-C stretching in the amorphous phase, emphasizing that these bands are sensitive to the crystallinity of PHB [Furukawa 2007, Bloembergen 1986, Bayari 2005]. In addition, the intensity of the band at 1722 cm^{-1} was found to increase (C=O in crystalline phase). Before the respirometry test, the 90/10 blend showed a band at 1735 cm^{-1} , which was assigned to C=O in a less organized crystalline phase [Conti 2006, Padermshoke 2005]. This phase underwent changes after the biotreatment, suggesting hydrolytic breaks of ester groups of the PHB fraction and some chain rearrangements. In the biotreated 70/30 blend, the band at 1742 cm^{-1} (C=O amorphous phase) was found to be absent, indicating consumption of carbonyl and consequent chain rearrangements of PHBV in contact with PE phase.

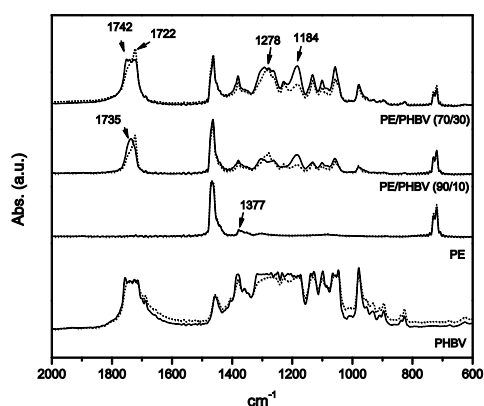


FIG. 2 FTIR OF THE FILMS BEFORE AND AFTER THE RESPIROMETRIC ASSAY.

The degree of crystallinity (% X_c) and the crystallite size (D) were calculated from XRD data extracted from Fig. 3. Crystallinity was calculated based on the ratio

of crystalline to amorphous peak areas. Crystallite size was calculated using Scherrer's equation [Munaro 2008], where B is the width at half height of the highest peak, θ is its angle position; k is a constant, which depends on particle size (spherical shape = 0.9) and λ is the X-ray length (Table 1).

The principal reflection peaks in the PHBV were at $2\theta = 13.30$ and 16.68° , corresponding to the (110) and (020) planes, emphasizing that the PHB (polyhydroxybutyrate) plane (110) also occurs at $2\theta \sim 16.8^\circ$. The PE planes (110) and (200) are located at $2\theta = 21.36$ and 23.62° , respectively.

After the biotreatment, the crystallite size (D) of the blends underwent modifications in the 110 plane, relative to the PHBV and PE fractions. In the PHBV fraction, the crystallite size decreased by about 7.5% in the 90/10 blend, due to the greater dispersion of PHBV domains in the PE matrix. However, in the 70/30 blend, the crystallite size of PHBV increased by 15%, because of the greater coalescence of the PHBV domains. The crystallite size in the PE fraction of the 90/10 and 70/30 blends increased by about 4.5% and 1.5%, respectively (Table 1), suggesting that in the blend containing the larger amount of synthetic polymer (PE), these chains underwent new crystallization on pre-existing crystals [Gonçalves 2009, Guadagno 2001]. The crystallite size in the biotreated PE showed a 2% decrease and the PHBV a 44% increase.

The degree of crystallinity (X_c) of PHBV decreased significantly (22 %) after 28 days buried in the soil, but increased by about 4% in PE after 180 days. The 90/10 blend showed an increase (8%) similar to that found in the PE films. The biotreated 70/30 blend showed an 8% decrease in X_c due to degradation of the PHBV crystalline fraction, represented by the (110) peak, which was assigned to HV chains.

The changes in the crystallite size of the PHBV and the 70/30 blend after the respirometric assay probably occurred due to biodegradation of the HV (valerate) chains, which caused the crystallite size to increase. Following Yoshie et al.'s model [2001], which proposes that PHBV is isodimorphic, i.e., the long sequences of HB (butyrate) units comprise the crystal core and the HV units comprise edges of the lamella, where the biodegradation process occurs. In the 70/30 blend, the larger and less organized interphases composed of flexible valerate units enable the biodegradation reactions. This was confirmed by the FTIR results, especially by the PHB bands sensitive to the degree of crystallinity, which underwent changes.

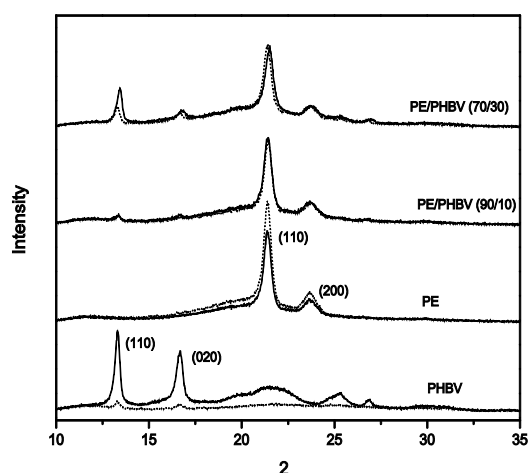


FIG. 3 XRD OF THE FILMS BEFORE AND AFTER THE RESPIROMETRIC ASSAY.

As shown in Fig. 2 (FTIR), branching PE presented a band relative to the short chains (methyl, ethyl, butyl). This PE underwent a break of the C-C and C-H bonds, which was facilitated by tertiary carbon, producing short chains after degradation [Corrales 2002]. In this experiment, PE began to biodegrade at around 120 days (respirometry data), suggesting that biodegradation started from the breaking of these weak bonds around the tertiary carbon, mainly in the amorphous phase, as reported in the literature [Volke-Sepulveda 2002, Suresh 2011]. In the 90/10 blend, which showed greater dispersion of PHBV in the PE matrix and smaller domains of PHBV, the degree of biodegradation was less (FTIR and XRD results).

TABLE 1 - CRYSTALLITES SIZE (D) AND CRYSTALLINITY DEGREE (%Xc) TO THE FILMS BEFORE AND AFTER THE RESPIROMETRIC ASSAY.

samples	D (nm) (110) PHBV		D (nm) (110) PE		% Xc	
	before	after	before	after	before	after
PHBV	4.2845	6.1802	---	---	60	47
PE	---	---	3.1373	3.0826	54	56
90/10	6.2920	5.8202	2.9977	3.1377	47	51
70/30	4.2851	4.9180	3.0369	3.0963	52	48

Fig. 4 shows micrographs of the films before and after the respirometric assay. The original films showed smooth surfaces (Fig. 4 a,c,e,g,i). After 28 days, the PHBV films showed craters and erosion on all the surfaces (Fig. 4 b). After 180 days of biotreatment, the PE films and blends displayed a few changes, such as grooving and exfoliation of surface layers, mainly in

the 70/30 blend.

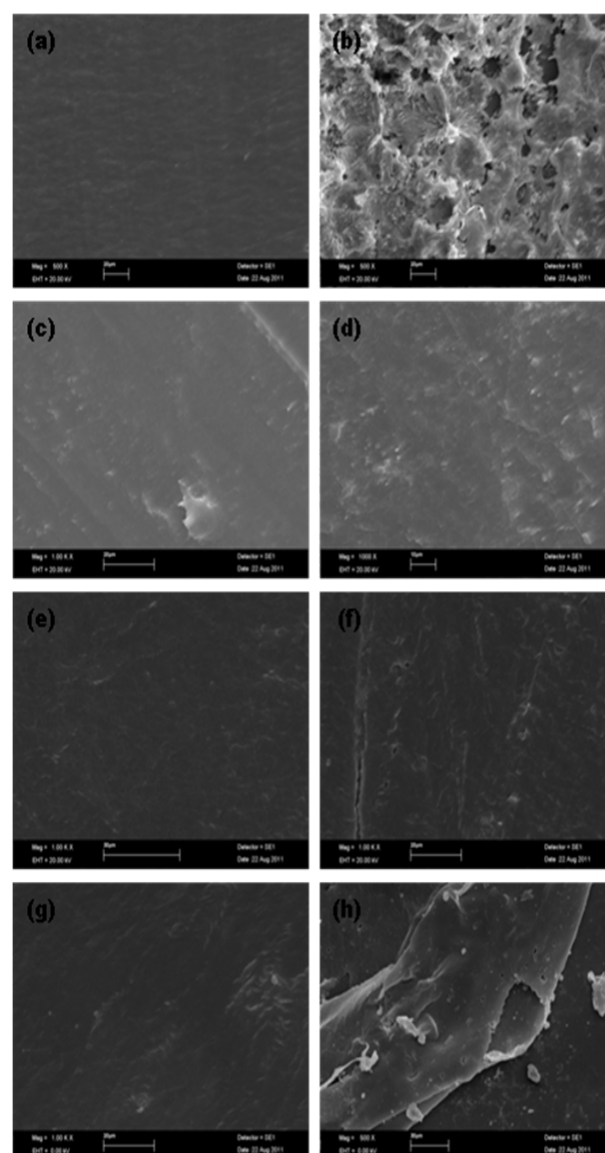


FIG. 4 FILMS SEM (A) PHBV BEFORE THE RESPIROMETRIC ASSAY; (B) PHBV AFTER 28 DAYS; (C) PE BEFORE; (D) PE AFTER 180 DAYS; (E) PE/PHBV 90/10 BEFORE; (F) PE/PHBV 90/10 AFTER; (G) PE/PHBV 70/30 BEFORE; (H) PE/PHBV 70/30 AFTER 180 DAYS.

The results of the biodegradation of blends indicated that the larger the proportion of biodegradable polymer was, the higher the biodegradation rate was. Thus, a large amount of PHBV results in a phase with larger domains of PHBV (more clusters), similar to what Oldak et al. [2005] found in their study who studied photodegradation and biodegradation of PE/cellulose blends, and concluded that blends with a higher proportion of cellulose (30%) formed larger domains, so that the interactions were not strong enough to prevent their degradation. In the 5-15% PE/cellulose blend, the cellulose disperses more homogeneously, with short inclusions in the PE matrix, facilitating the intermolecular interactions and

hindering biodegradation. This effect was reported by Borah & Chaki [2011] who used a blend of low density polyethylene/methyl ethylene-co-acrylate and found two phases, with the minor component (cellulose) dispersed in the main continuous matrix (PE).

Thus, in the present study, the higher the proportion of PHB in the blend was, the larger the interphase between the polymers was, which was considered an intermediate and less organized phase where biodegradation occurred preferentially. The changes observed in PHBV and PE/PHBV blends were attributed to the action of microorganisms that catalyzed hydrolytic reactions of PHBV ester groups at the interface between crystalline and amorphous phases (in PHBV) and in interphases (intermediate regions between PE and PHBV in the blend). Hence, the larger the interphase was, the greater the probability of the occurrence of biodegradation was (as in the case of the 70/30 blend).

Conclusions

Blends containing higher proportions of PHBV showed higher susceptibility to microbial degradation in soil, due to the distribution of the larger phases (PHBV) in contact with the PE matrix (interphase). The samples biodegraded in the following sequence: PHBV > PE/PHBV 70/30 > PE/PHBV 90/10 > PE.

The microbial action occurred through the hydrolysis of PHBV ester groups (at the interface between amorphous and crystalline phases) and in interphases in the blend (contact between the two different polymers).

CO₂ evolution (respirometry) is an efficient method to assess the biodegradation of polymer films, particularly when allied to FTIR, XRD and SEM techniques.

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